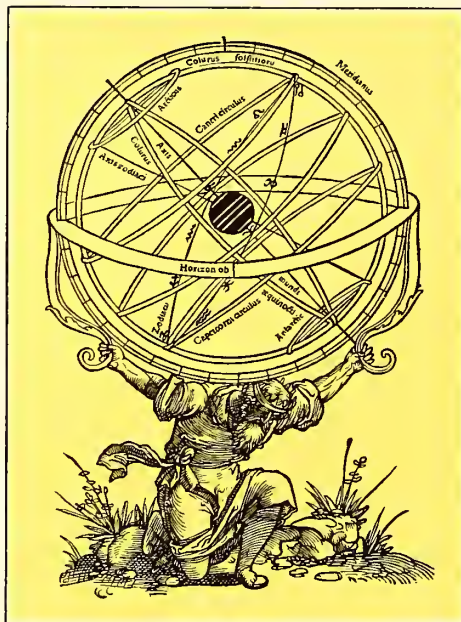




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II. *Experimental Researches in Electricity*.—*Sixteenth Series*.

By MICHAEL FARADAY, *Esq., D.C.L. F.R.S. Fullerian Prof. Chem. Royal Institution, Corr. Memb. Royal and Imp. Acadd. of Sciences, Paris, Petersburg, Florence, Copenhagen, Berlin, Göttingen, Modena, Stockholm, &c. &c.*

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§ 24. *On the source of power in the voltaic pile.*

- ¶ i. *Exciting electrolytes, &c. being conductors of thermo and feeble currents.*
- ¶ ii. *Inactive conducting circles containing an electrolytic fluid.*
- ¶ iii. *Active circles excited by solution of sulphuret of potassium, &c.*

§ 24. *On the source of power in the voltaic pile.*

1796. **WHAT** is the source of power in a voltaic pile? This question is at present of the utmost importance in the theory and to the development of electrical science. The opinions held respecting it are various; but by far the most important are the two which respectively find the source of power in contact, and in chemical force. The question between them touches the first principles of electrical action; for the opinions are in such contrast, that two men respectively adopting them are thenceforward constrained to differ, in every point, respecting the probable and intimate nature of the agent or force on which all the phenomena of the voltaic pile depend.

1797. The theory of contact is the theory of VOLTA, the great discoverer of the voltaic pile itself, and it has been sustained since his day by a host of philosophers, amongst whom, in recent times, rank such men as PFAFF, MARIANINI, FECHNER, ZAMBONI, MATTEUCCI, KARSTEN, BOUCHARDAT, and as to the excitement of the power, even DAVY; all bright stars in the exalted regions of science. The theory of chemical action was first advanced by FABRONI\*, WOLLASTON†, and PARROT‡, and has been more or less developed since by CÆRSTED, BECQUEREL, DE LA RIVE, RITCHIE, POUILLET, SCHÖENBEIN, and many others, amongst whom BECQUEREL ought to be distinguished as having contributed, from the first, a continually increasing mass of the strongest

\* A.D. 1792, 1799. BECQUEREL's *Traité de l'Électricité*, i. pp. 81—91, and NICHOLSON's *Quarto Journal*, iii. 308. iv. 120, or *Journal de Physique*, vi. 348.

† A.D. 1801. *Philosophical Transactions*, 1801, p. 427.

‡ A.D. 1801. *Annales de Chimie*, 1829, xlii. 45; 1831, xlv. 361.

experimental evidence in proof that chemical action always evolves electricity\*; and DE LA RIVE should be named as most clear and constant in his views, and most zealous in his production of facts and arguments, from the year 1827 to the present time†.

1798. Examining this question by the results of definite electro-chemical action, I felt constrained to take part with those who believed the origin of voltaic power to consist in chemical action alone (875. 965.), and ventured a paper on it in April 1834‡ (875, &c.), which obtained the especial notice of MARIANINI§. The rank of this philosopher, the observation of FECHNER||, and the consciousness that over the greater part of Italy and Germany the contact theory still prevailed, have induced me to re-examine the question most carefully. I wished not merely to escape from error, but was anxious to convince myself of the truth of the contact theory; for it was evident that if contact electromotive force had any existence, it must be a power not merely unlike every other natural power as to the phenomena it could produce, but also in the far higher points of limitation, definite force, and finite production (2065.).

1799. I venture to hope that the experimental results and arguments which have been thus gathered may be useful to science. I fear the detail will be tedious, but that is a necessary consequence of the state of the subject. The contact theory has long had possession of men's minds, is sustained by a great weight of authority, and for years had almost undisputed sway in some parts of Europe. If it be an error, it can only be rooted out by a great amount of forcible experimental evidence; a fact sufficiently clear to my mind by the circumstance, that DE LA RIVE's papers have not already convinced the workers upon this subject. Hence the reason why I have thought it needful to add my further testimony to his and that of others, entering into detail and multiplying facts in a proportion far beyond any which would have been required for the proof and promulgation of a new scientific truth (2017.). In so doing, I may occasionally be only enlarging, yet then I hope strengthening, what others, and especially DE LA RIVE, have done.

1800. It will tend to clear the question, if the various views of contact are first stated. VOLTA's theory is, that the simple contact of conducting bodies causes electricity to be developed at the point of contact without any change in nature of the bodies themselves; and that though such conductors as water and aqueous fluids

\* A.D. 1824, &c. *Annales de Chimie*, 1824, xxv. 405; 1827, xxxv. 113; 1831, xlv. 265, 276, 337, xlvii. 113, xlix. 131.

† Ibid. 1828, xxxvii. 225, xxxix. 297; 1836, lxii. 147: or *Mémoires de Genève*, 1829, iv. 285; 1832, vi. 149; 1835, vii.

‡ *Philosophical Transactions*, 1834, p. 425.

§ *Memorie della Società Italiana in Modena*, 1837, xxi. p. 205.

|| *Philosophical Magazine*, 1838, xiii. 205; or *POGGENDORF's Annalen*, xlii. p. 481. FECHNER refers also to PFAFF's reply to my paper. I never cease to regret that the German is a sealed language to me.

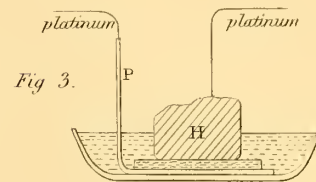
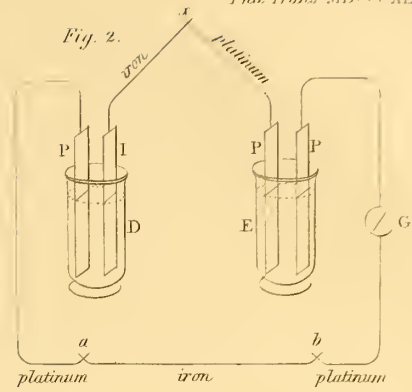
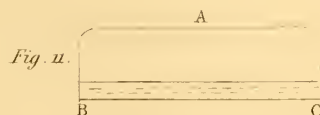
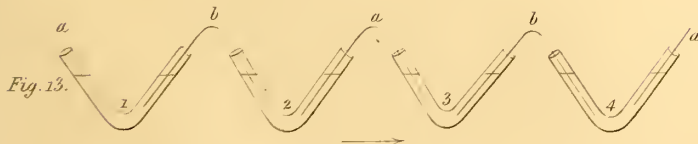
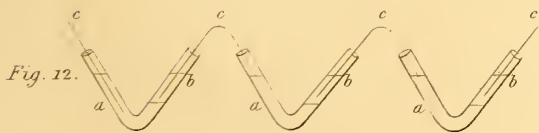
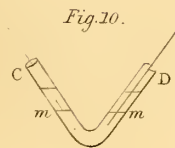
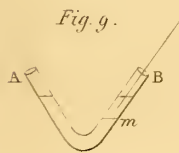
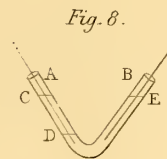
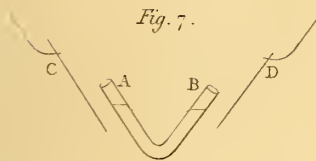
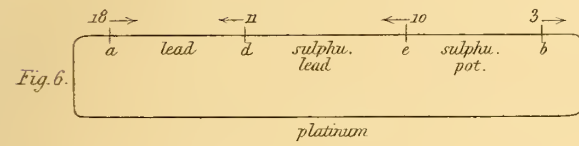
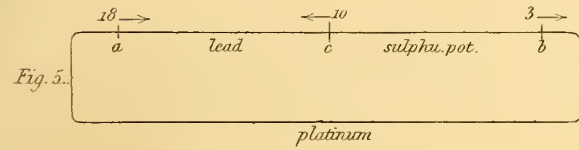
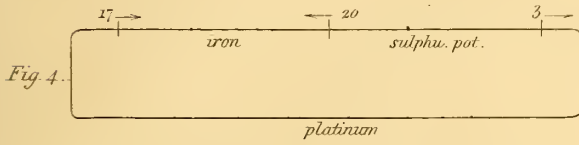
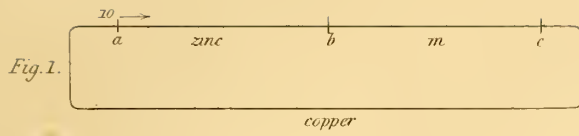
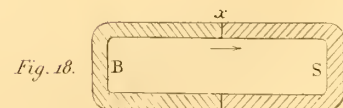
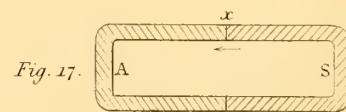
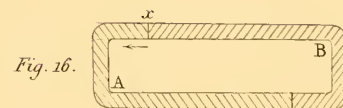
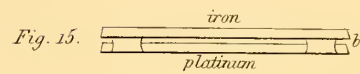
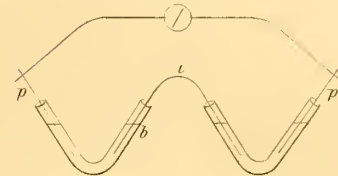


Fig. 14.







have this property, yet the degree in which they possess it is unworthy of consideration in comparison with the degree to which it rises amongst the metals\*. The present views of the Italian and German contact philosophers are, I believe, generally the same, except that occasionally more importance is attached to the contact of the imperfect conductors with the metals. Thus ZAMBONI (in 1837) considers the metallic contact as the most powerful source of electricity, and not that of the metals with the fluids†; but KARSTEN, holding the contact theory, transfers the electromotive force to the contact of the fluids with the solid conductors‡. MARIANINI holds the same view of the principle of contact, with this addition, that actual contact is not required to the exertion of the exciting force, but that the two approximated dissimilar conductors may affect each other's state, when separated by sensible intervals of the  $\frac{1}{100000}$ th of a line and more, air intervening§.

1801. DE LA RIVE, on the contrary, contends for simple and strict chemical action, and, as far as I am aware, admits of no current in the voltaic pile that is not conjoined with and dependent upon a complete chemical effect. That admirable electrician BECQUEREL, though expressing himself with great caution, seems to admit the possibility of chemical attractions being able to produce electrical currents when they are not strong enough to overcome the force of cohesion, and so terminate in combination||. SCHÖENBEIN states that a current may be produced by a tendency to chemical action, i. e. that substances which have a tendency to unite chemically may produce a current, though that tendency is not followed up by the actual combination of the substances¶. In these cases the assigned force becomes the same as the contact of VOLTA, inasmuch as the acting matters are not altered whilst producing the current. DAVY's opinion was, that contact like that of VOLTA excited the current or was the cause of it, but that chemical changes supplied the current. For myself I am at present of the opinion which DE LA RIVE holds, and do not think that, in the voltaic pile, mere contact does anything in the excitation of the current, except as it is preparatory to, and ends in, complete chemical action (1741. 1745.).

1802. Thus the views of contact vary, and it may be said that they pass gradually from one to another, even to the extent of including chemical action: but the two extremes appear to me irreconcilable in principle under any shape; they are as follows. The contact theory assumes, that when two different bodies being conductors of electricity are in contact, there is a force at the point of contact by which one of the bodies gives a part of its natural portion of electricity to the other body, which the latter takes in addition to its own natural portion; that, though the touching points have thus respectively given and taken electricity, they cannot retain the charge which their contact has caused, but discharge their electricities to the masses

\* Annales de Chimie, 1802, xl. p. 225.

† Bibliothèque Universelle, 1836, v. 387; 1837, viii. 189.

‡ L'Institut, No. 150.

§ Mem. della Soc. Ital. in Modena, 1837, xxi. 232-237.

|| Annales de Chimie, 1835, lx. 171; and Traité de l'Électricité, i. pp. 253, 258.

¶ Philosophical Magazine, 1838, xii. 227, 311, 314; also Bibliothèque Universelle, 1838, xiv. 155, 395.

respectively behind them (2067.): that the force which, at the point of contact, induces the particles to assume a new state, cannot enable them to keep that state (2069.): that all this happens without any permanent alteration of the parts that are in contact, and has no reference to their chemical forces (2065. 2069.).

1803. The chemical theory assumes, that at the place of action, the particles which are in contact act chemically upon each other and are able, under the circumstances, to throw more or less of the acting force into a dynamic form (947. 996. 1120.): that in the most favourable circumstances, the whole is converted into dynamic force (1000.): that then the amount of current force produced is an exact equivalent of the original chemical force employed; and that in no case (in the voltaic pile) can any electric current be produced, without the active exertion and consumption of an equal amount of chemical force, ending in a given amount of chemical change.

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1804. MARIANINI's paper\* was to me a great motive for re-examining the subject; but the course I have taken was not so much for the purpose of answering particular objections, as for the procuring evidence, whether relating to controverted points or not, which should be satisfactory to my own mind, open to receive either one theory or the other. This paper, therefore, is not controversial, but contains further facts and proofs of the truth of DE LA RIVE's views. The cases MARIANINI puts are of extreme interest, and all his objections must, one day, be answered, when numerical results, both as to intensity and quantity of force, are obtained; but they are all debatable, and, to my mind, depend upon variations of quantity which do not affect seriously the general question. Thus, when that philosopher quotes the numerical results obtained by considering two metals with fluids at their opposite extremities which tend to form counter currents, the difference which he puts down to the effect of metallic contact, either made or interrupted, I think accountable for, on the facts partly known respecting opposed currents; and with me differences quite as great, and greater, have arisen, and are given in former papers (1046.), when metallic contacts were in the circuit. So at page 213 of his memoir, I cannot admit that  $e$  should give an effect equal to the difference of  $b$  and  $d$ ; for in  $b$  and  $d$  the opposition presented to the excited currents is merely that of a bad conductor, but in the case of  $e$  the opposition arises from the power of an opposed acting source of a current.

1805. As to the part of his memoir respecting the action of sulphuretted solutions†, I hope to be allowed to refer to the investigations made further on. I do not find, as the Italian philosopher, that iron with gold or platina, in solution of the sulphuret of potassa, is positive to them‡, but, on the contrary, powerfully negative, and for reasons given in the sequel (2049.).

1806. With respect to the discussion of the cause of the spark before contact§,

\* Memorie della Società Italiana in Modena, 1827, xxi. p. 205.

† Ibid. p. 217.

‡ Ibid. p. 217.

§ Ibid. p. 225.



MARIANINI admits the spark, but I give it up altogether. JACOBI's paper\* convinces me I was in error as to *that proof* of the existence of a state of tension in the metals before contact (915. 956.). I need not therefore do more at present than withdraw my own observations.

1807. I now proceed to address myself to the general argument, rather than to particular controversy, or to the discussion of cases feeble in power and doubtful in nature; for I have been impressed from the first with the feeling that it is no weak influence or feeble phenomenon that we have to account for, but such as indicates a force of extreme power, requiring, therefore, that the cause assigned should bear some proportion, both in intensity and quantity, to the effects produced.

1808. The investigations have all been made by aid of currents and the galvanometer, for it seemed that such an instrument and such a course were best suited to an examination of the electricity of the voltaic pile. The electrometer is no doubt a most important instrument, but the philosophers who do use it are not of accord in respect to the safety and delicacy of its results. And even if the few indications as yet given by the electrometer be accepted as correct, they are far too general to settle the question of, whether contact or chemical action is the exciting force in the voltaic battery. To apply that instrument closely and render it of any force in supplying affirmative arguments to either theory, it would be necessary to construct a table of contacts, or the effects of contacts, of the different metals and fluids concerned in the construction of the voltaic pile, taken in pairs (1868.), expressing in such table both the *direction* and the *amount* of the contact force.

1809. It is assumed by the supporters of the contact theory, that though the metals exert strong electromotive forces at their points of contact with each other, yet these are so balanced in a metallic circuit that no current is ever produced whatever their arrangement may be. So in Plate III. fig. 1. if the contact force of copper and zinc is  $10 \longrightarrow$ , and a third metal be introduced at *m*, the effect of its contacts, whatever that metal may be, with the zinc and copper at *b* and *c*, will be an amount of force in the opposite direction =  $10$ . Thus, if it were potassium, its contact force at *b* might be  $5 \longrightarrow$ , but then its contact force at *c* would be  $\longleftarrow 15$ : or if it were gold, its contact force at *b* might be  $\longleftarrow 19$ , but then its contact force at *c* would be  $9 \longrightarrow$ . This is a very large assumption, and that the theory may agree with the facts is necessary: still it is, I believe, only an assumption, for I am not aware of any data, independent of the theory in question, which prove its truth.

1810. On the other hand, it is assumed that fluid conductors, and such bodies as contain water, or, in a word, those which I have called electrolytes (664. 823. 921.), either exert no contact force at their place of contact with the metals, or if they do exert such a power, then it is with this most important difference, that the forces are not subject to the same law of compensation or neutralization in the complete circuit, as holds with the metals (1809.). But this, I think I am justified in saying, is an as-

\* Philosophical Magazine, 1838, xiii. 401.

sumption also, for it is supported not by any independent measurement or facts (1808.), but only by the theory which it is itself intended to support.

1811. Guided by this opinion, and with a view to ascertain what is, in an active circle, effected by contact and what by chemical action, I endeavoured to find some bodies in this latter class (1810.) which should be without chemical action on the metals employed, so as to exclude that cause of a current, and yet such good conductors of electricity as to show any currents due to the contact of these metals with each other or with the fluid: concluding that any electrolyte which would conduct the thermo current of a single pair of bismuth and antimony plates would serve the required purpose, I sought for such, and fortunately soon found them.

¶ i. *Exciting electrolytes, &c., being conductors of thermo and feeble currents.*

1812. *Sulphuret of potassium.*—This substance and its solution were prepared as follows. Equal weights of caustic potash (potassa fusa) and sulphur were mixed and heated gradually in a Florence flask, till the whole had fused and united, and the sulphur in excess began to sublime. It was then cooled and dissolved in water, so as to form a strong solution, which by standing became quite clear.

1813. A portion of this solution was included in a circuit containing a galvanometer and a pair of antimony and bismuth plates; the connexion with the electrolyte was made by two platinum plates, each about two inches long and half an inch wide: nearly the whole of each was immersed, and they were about half an inch apart. When the circuit was completed, and all at the same temperature, there was no current; but the moment the junction of the antimony and bismuth was either heated or cooled, the corresponding thermo current was produced, causing the galvanometer-needle to be permanently deflected, occasionally as much as  $80^{\circ}$ . Even the small difference of temperature occasioned by touching the SEEBECK element with the finger, produced a very sensible current through the electrolyte. When in place of the antimony-bismuth combination mere wires of *copper and platinum*, or *iron and platinum* were used, the application of the spirit-lamp to the junction of these metals produced a thermo current which instantly travelled round the circuit.

1814. Thus this electrolyte will, as to high conducting power, fully answer the condition required (1811.). It is so excellent in this respect, that I was able to send the thermo current of a single SEEBECK's element across five successive portions connected with each other by platinum plates.

1815. *Nitrous acid.*—Yellow anhydrous nitrous acid, made by distilling dry nitrate of lead, being put into a glass tube and included in a circuit with the antimony-bismuth arrangement and the galvanometer, gave no indication of the passage of the thermo current, though the immersed electrodes consisted each of about four inches in length of moderately thick platinum wire, and were not above a quarter of an inch apart.

1816. A portion of this acid was mixed with nearly its volume of pure water; the



resulting action caused depression of temperature, the evolution of some nitrous gas, the formation of some nitric acid, and a dark green fluid was produced. This was now such an excellent conductor of electricity, that almost the feeblest current could pass it. That produced by SEEBECK'S circle was sensible when only one eighth of an inch in length of the platinum wires dipped in the acid. When a couple of inches of each electrode was in the fluid, the conduction was so good, that it made very little difference at the galvanometer whether the platinum wires touched each other in the fluid, or were a quarter of an inch apart\*.

1817. *Nitric acid*.—Some pure nitric acid was boiled to drive off all the nitrous acid, and then cooled. Being included in the circuit by platinum plates (1813.), it was found to conduct so badly that the effect of the antimony-bismuth pair, when the difference of temperature was at the greatest, was scarcely perceptible at the galvanometer.

1818. On using a pale yellow acid, otherwise pure, it was found to possess rather more conducting power than the former. On employing a red nitric acid, it was found to conduct the thermo-current very well. On adding some of the green nitrous acid (1816.) to the colourless nitric acid, the mixture acquired high conducting powers. Hence it is evident that nitric acid is not a good conductor when pure, but that the presence of nitrous acid in it (conjointly probably with water), gives it this power in a very high degree amongst electrolytes†. A very red strong nitric acid, and a weak green acid, (consisting of one vol. strong nitric acid and two vols. of water, which had been rendered green by the action of the negative platinum electrode of a voltaic battery,) were both such excellent conductors that the thermo current could pass across five separate portions of them connected by platinum plates, with so little retardation that I believe twenty interruptions would not have stopped this feeble current.

1819. *Sulphuric acid*.—Strong oil of vitriol, when between platinum electrodes (1813.), conducted the antimony-bismuth thermo current sensibly, but feebly. A mixture of two volumes acid and one volume water conducted much better, but not nearly so well as the two former electrolytes (1814. 1816.). A mixture of one volume of oil of vitriol and two volumes saturated solution of sulphate of copper conducted this feeble current very fairly.

*Potassa*.—A strong solution of caustic potassa, between platinum plates, conducted the thermo current sensibly, but very feebly.

1820. I will take the liberty of describing here, as the most convenient place, other

\* DE LA RIVE has pointed out the facility with which an electric current passes between platinum and nitrous acid. *Annales de Chimie*, 1828, xxxvii. 278.

† SCHÖENBEIN'S experiments on a compound of nitric and nitrous acids will probably bear upon and illustrate this subject. *Bibliothèque Universelle*, 1817, x. 406.

results relating to the conducting power of bodies, which will be required hereafter in these investigations. Galena, yellow sulphuret of iron, arsenical pyrites, native sulphuret of copper and iron, native gray artificial sulphuret of copper, sulphurets of bismuth, iron, and copper, globules of oxide of burnt iron, oxide of iron by heat or scale oxide, conducted the thermo current very well. Native peroxide of manganese and peroxide of lead conducted it moderately well.

1821. The following are bodies, in some respect analogous in nature and composition, which did not sensibly conduct this weak current when the contact surfaces were small. Artificial gray sulphuret of tin, blende, cinnabar, hæmatite, Elba iron-ore, native magnetic oxide of iron, native peroxide of tin or tinstone, wolfram, fused and cooled protoxide of copper, peroxide of mercury.

1822. Some of the foregoing substances are very remarkable in their conducting power. This is the case with the solution of sulphuret of potassium (1813.) and the nitrous acid (1816.), for the great amount of this power. The peroxide of manganese and lead are still more remarkable for possessing this power, because the *protoxides* of these metals do not conduct either the feeble thermo current or a far more powerful one from a voltaic battery. This circumstance made me especially anxious to verify the point with the peroxide of lead. I therefore prepared some from red-lead by the action of successive portions of nitric acid, then boiled the brown oxide, so obtained, in several portions of distilled water, for days together, until every trace of nitric acid and nitrate of lead had been removed; after which it was well and perfectly dried. Still, when a heap of it in powder, and consequently in very imperfect contact throughout its own mass, was pressed between two plates of platinum and so brought into the thermo-electric circuit (1813.), the current was found to pass readily.

¶ ii. *Inactive conducting circles containing a fluid or electrolyte.*

1823. DE LA RIVE has already quoted the case of potash, iron and platina\*, to show that where there was no chemical action there was no current. My object is to increase the number of such cases; to use other fluids than potash, and such as have good conducting power for weak currents; to use also strong and weak solutions; and thus to accumulate the conjoint experimental and argumentative evidence by which the great question must finally be decided.

1824. I first used the sulphuret of potassium as an electrolyte of good conducting power, but chemically inactive (1811.) when associated with iron and platinum in a circuit. The arrangement is given in fig. 2, where D, E represent two test-glasses containing the strong solution of sulphuret of potassium (1812.); and also four metallic plates, about 0.5 of an inch wide and two inches long in the immersed part, of which the three marked P, P, P were platinum, and that marked I, of clean iron: these were connected by iron and platinum wires, as in fig. 2., a galvanometer being

\* Philosophical Magazine, 1837, xi. 275.



introduced at G. In this arrangement there were three metallic contacts of platinum and iron,  $a$   $b$  and  $x$ : the two first being opposed to each other, may be considered as neutralizing each other's forces; but the third, being unopposed by any other metallic contact, can be compared with either the difference of  $a$  and  $b$  when one is warmer than the other, or with itself when in a heated or cooled state (1830.), or with the force of chemical action when any body capable of such action is introduced there (1831.).

1825. When this arrangement is completed and in order, there is absolutely no current circulating through it, and the galvanometer-needle rests at  $0^\circ$ ; yet is the whole circuit open to a very feeble current, for a difference of temperature at any one of the junctions  $a$ ,  $b$ , or  $x$ , causes a corresponding thermo current, which is instantly detected by the galvanometer, the needle standing permanently at  $30^\circ$  or  $40^\circ$ , or even  $50^\circ$ .

1826. But to obtain this proper and normal state, it is necessary that certain precautions be attended to. In the first place, if the circuit be complete in every part except for the immersion of the iron and platinum plates into the cup D, then, upon their introduction, a current will be produced directed from the platinum (which appears to be positive) through the solution to the iron; this will continue perhaps five or ten minutes, or if the iron has been carelessly cleaned, for several hours; it is due to an action of the sulphuretted solution on *oxide of iron*, and not to any effect on the metallic iron; and when it has ceased, the disturbing cause may be considered as exhausted. The experimental proofs of the truth of this explanation, I will quote hereafter (2049.).

1827. Another precaution relates to the effect of accidental movements of the plates in the solution. If two platinum plates be put into a solution of this sulphuret of potassium, and the circuit be then completed, including a galvanometer, the arrangement, if perfect, will show no current; but if one of the plates be lifted up into the air for a few seconds and then replaced, it will be negative to the other, and produce a current lasting for a short time\*. If the two plates be iron and platinum, or of any other metal or substance not acted on by the sulphuret, the same effect will be produced. In these cases, the current is due to the change wrought by the air on the film of sulphuretted solution adhering to the removed plate†; but a far less cause than this will produce a current, for if one of the platinum plates be removed, washed well, dried, and even heated, it will, on its reintroduction, almost certainly exhibit the negative state for a second or two.

1828. These or other disturbing causes appear the greater in these experiments in

\* MARIANINI observed effects of this kind produced by exposure to the air, of one of two plates dipped in nitric acid. *Annales de Chimie*, 1830, xlv. p. 42.

† BECQUEREL long since referred to the effect of such exposure of a plate, dipped in certain solutions, to the air. Generally the plate so exposed became positive on re-immersion. *Annales de Chimie*, 1824, xxv. 405.

consequence of the excellent conducting power of the solution used; but they do not occur if care be taken to avoid any disturbance of the plates or the solution, and then, as before said, the whole acquires a normal and perfectly inactive state.

1829. Here then is an arrangement in which the contact of platinum and iron at  $x$  is at liberty to produce any effect which such a contact may have the power of producing; and yet what is the consequence? absolutely nothing. This is not because the electrolyte is so bad a conductor that a current of contact cannot pass, for currents far feebler than this is assumed to be, pass readily (1813.); and the electrolyte employed is vastly superior in conducting power to those which are commonly used in voltaic batteries or circles, in which the current is still assumed to be dependent upon contact. The simple conclusion to which the experiment should lead is, in my opinion, that the contact of iron and platinum is absolutely without any electromotive force (1835. 1859. 1889.).

1830. If the contact be made really active and effective, according to the beautiful discovery of SEEBECK, by making its temperature different to that of the other parts of the circuit, then its power of generating a current is shown (1824.). This enables us to compare the supposed power of the mere contact with that of a thermo contact; and we find that the latter comes out as infinitely greater than the former, for the former is nothing. The same comparison of mere contact and thermo contact may be made by contrasting the effect of the contact  $c$  at common temperatures, with either the contact at  $a$  or at  $b$ , either heated or cooled. Very moderate changes of temperature at these places produce instantly the corresponding current, but the mere contact at  $x$  does nothing.

1831. So also I believe that a true and philosophic and even rigid comparison may be made at  $x$ , between the assumed effect of mere contact and that of chemical action. For if the metals at  $x$  be separated, and a piece of paper moistened in dilute acid, or a solution of salt, or if only the tongue or a wet finger be applied there, then a current is caused, stronger by far than the thermo-currents before produced (1830.), passing from the iron through the introduced acid or other active fluid to the platinum. This is a case of current from chemical action without any metallic contact in the circuit on which the effect can for a moment be supposed to depend (879.); it is even a case where metallic contact is changed for chemical action, with the result, that where contact is found to be quite ineffectual, chemical action is very energetic in producing a current.

1832. It is of course quite unnecessary to say that the same experimental comparisons may be made at either of the other contacts,  $a$  or  $b$ .

1833. Admitting for the moment that the arrangement proves that the contact of platinum and iron at  $x$  has no electromotive force (1835. 1859.), then it follows also that the contact of either platinum or iron with any other metal has no such force. For if another metal, as zinc, be interposed between the iron and platinum at  $x$ , fig. 2,



no current is produced; and yet the test application of a little heat at *a* or *b*, will show by the corresponding current, that the circuit being complete will conduct any current that may tend to pass. Now that the contacts of zinc with iron and with platinum are of equal electromotive force, is not for a moment admitted by those who support the theory of contact activity; we ought therefore to have a resulting action equal to the differences of the two forces, producing a certain current. No such current is produced, and I conceive, with the admission above, that such a result proves that the contacts *iron-zinc* and *platinum-zinc* are entirely without electromotive force.

1834. Gold, silver, potassium, and copper were introduced at *x* with the like negative effect; and so no doubt might every other metal, even according to the relation admitted amongst the metals by the supporters of the contact theory (1809.). The same negative result followed upon the introduction of many other conducting bodies at the same place; as, for instance, those already mentioned as easily conducting the thermo current (1820.); and the effect proves, I think, that the contact of any of these with either iron or platinum is utterly ineffective as a source of electromotive force.

1835. The only answer which, as it appears to me, the contact theory can set up in opposition to the foregoing facts and conclusions is, to say that the solution of sulphuret of potassium in the cup D, fig. 2, acts as a metal would do (1809.), and so the effects of all the contacts in the circuit are exactly balanced. I will not stop at this moment to show that the departure with respect to electrolytes, or the fluid bodies in the voltaic pile, *from the law* which is supposed to hold good with the metals and solid conductors, though only an assumption, is still essential to the contact theory of the voltaic pile (1810. 1861.)\*; nor to prove that the electrolyte is no otherwise like the metals than in having no contact electromotive force whatever. But believing that this will be very evident shortly, I will go on with the experimental results, and resume these points hereafter (1859. 1889.).

1836. The experiment was now repeated with the substitution of a bar of *nickel* for that of iron, fig. 2 (1824.), all other things remaining the same†. The circuit was again found to be a good conductor of a feeble thermo current, but utterly inefficient as a voltaic circuit when all was at the same temperature, and due precautions taken (2051.). The introduction of metals at the contact *x* was as ineffective as before (1834.); the introduction of chemical action at *x* was as striking in its influence as in the former case (1831.); all the results were, in fact, parallel to

\* See FECHNER'S words. Philosophical Magazine, 1838, xiii. 377.

† There is another form of this experiment which I sometimes adopted, in which the cup E, fig. 2, with its contents, was dismissed, and the platinum plates in it connected together. The arrangement may then be considered as presenting three contacts of iron and platinum, two acting in one direction, and one in the other. The arrangement and the results are virtually the same as those already given. A still simpler but equally conclusive arrangement for many of the arguments, is to dismiss the iron between *a* and *b* altogether, and so have but one contact, that at *x*, to consider.

those already obtained; and if the reasoning then urged was good, it will now follow that the contact of platinum and nickel with each other, or of either with any of the different metals or solid conductors introduced at  $x$ , is entirely without electromotive force\*.

1837. Many other pairs of metals were compared together in the same manner; the solution of sulphuret of potassium connecting them together at one place, and their mutual contact doing that office at another. The following are cases of this kind: iron and gold; iron and palladium; nickel and gold; nickel and palladium; platina and gold; platina and palladium. In all these cases the results were the same as those already given with the combinations of platinum and iron.

1838. It is necessary that due precaution be taken to have the arrangements in an unexceptionable state. It often happened that the first immersion of the plates gave deflections; it is, in fact, almost impossible to put two plates of the *same metal* into the solution without causing a deflection; but this generally goes off very quickly, and then the arrangement may be used for the investigation (1826.). Sometimes there is a feeble but rather permanent deflection of the needle; thus when platinum and palladium were the metals, the first effect fell and left a current able to deflect the galvanometer-needle  $3^\circ$ , indicating the platinum to be positive to the palladium. This effect of  $3^\circ$ , however, is almost nothing compared to what a mere thermo current can cause, the latter producing a deflection of  $60^\circ$  or more; besides which, even supposing it an essential effect of the arrangement, it is in the wrong direction for the contact theory. I rather incline to refer it to that power which platinum and other substances have of effecting combination and decomposition without themselves entering into union; and I have occasionally found that when a platinum plate has been left for some hours in a strong solution of sulphuret of potassium (1812.) a small quantity of sulphur has been deposited upon it. Whatever the cause of the final feeble current may be, the effect is too small to be of any service in support of the contact theory; while, on the other hand, it affords delicate and, therefore, strong indications in favour of the chemical theory.

1839. A change was made in the form and arrangement of the cup D, fig. 2, so as to allow of experiments with other bodies than the metals. The solution of sulphuret of potassium was placed in a shallow vessel, the platinum plate was bent so that the immersed extremity corresponded to the bottom of the vessel; on this a piece of loosely folded cloth was laid in the solution, and on that again the mineral or other substance to be compared with the platinum; the fluid being of such depth that only part of that substance was in it, the rest being clean and dry; on this portion the platinum wire, which completed the circuit, rested. The arrangement of this part of

\* One specimen of nickel was, on its immersion, positive to platinum for seven or eight minutes, and then became neutral. On taking it out it seemed to have a yellowish tint on it, as if invested by a coat of sulphuret; and I suspected this piece had acted like lead (1885.) and bismuth (1895.). It is difficult to get pure and also perfectly compact nickel; and if porous, then the matter retained in the pores produces currents.



the circuit is given in section at fig. 3, where H represents a piece of galena to be compared with the platinum P.

1840. In this way galena, compact yellow copper pyrites, yellow iron pyrites, and globules of oxide of burnt iron, were compared with platinum, (the solution of sulphuret of potassium being the electrolyte used in the circuit,) and with the same results as were before obtained with metals (1829. 1833.).

1841. Experiments hereafter to be described gave arrangements in which, with the same electrolyte, sulphuret of lead was compared with gold, palladium, iron, nickel, and bismuth (1885. 1886.); also sulphuret of bismuth with platinum, gold, palladium, iron, nickel, lead, and sulphuret of lead (1894.), and always with the same result. Where no chemical action occurred there no current was formed; although the circuit remained an excellent conductor, and the contact existed by which, it is assumed in the contact theory, such a current should be produced.

1842. Instead of the strong solution, a dilute solution of the yellow sulphuret of potassium, consisting of one volume of strong solution (1812.) and ten volumes of water, was used. Plates of platinum and iron were arranged in this fluid as before (1824.); at first the iron was negative (2049.), but in ten minutes it was neutral, and the needle at  $0^{\circ}$ \*. Then a weak chemical current excited at  $x$  (1831.) easily passed; and even a thermo current (1830.) was able to show its effects at the needle. Thus a strong or a weak solution of this electrolyte showed the same phenomena. By diluting the solution still further, a fluid could be obtained in which the iron was, after the first effect, permanently but feebly positive. On allowing time, however, it was found that in all such cases black sulphuret formed here and there on the iron. Rusted iron was negative to platinum (2049.) in this very weak solution, which by direct chemical action could render metallic iron positive.

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1843. In all the preceding experiments the electrolyte used has been the sulphuret of potassium solution; but I now changed this for another, very different in its nature, namely, the *green nitrous acid* (1816.), which has already been shown to be an excellent conductor of electricity. Iron and platinum were the metals employed, both being in the form of wires. The vessel in which they were immersed was a tube like that formerly described (1815.); in other respects the arrangement was the same in principle as those already used (1824. 1836.). The first effect was the production of a current, the iron being positive in the acid to the platina; but this *quickly ceased*, and the galvanometer-needle came to  $0^{\circ}$ . In this state, however, the circuit could not in all things be compared with the one having the solution of sulphuret of

\* Care was taken in these and the former similar cases to discharge the platinum surface of any reacting force it might acquire from the action of the previous current, by separating it from the other metals, and touching it in the liquid for an instant with another platinum plate.

potassium for its electrolyte (1824.); for although it could conduct the thermo current of antimony and bismuth in a certain degree, yet that degree was very small compared to the power possessed by the former arrangement, or to that of a circle in which the nitrous acid was between two platinum plates (1816.). This remarkable retardation is consequent upon the assumption by the iron of that peculiar state which SCHÖENBEIN has so well described and illustrated by his numerous experiments and investigations. But though it must be admitted that the iron in contact with the acid is in a peculiar state (1951. 2001. 2033.), yet it is also evident that a circuit consisting of platinum, iron, peculiar iron, and nitrous acid, does not cause a current though it have sufficient conducting power to carry a thermo current.

1844. But if the contact of platinum and iron has an electromotive force, why does it not produce a current? The application of heat (1830.), or of a little chemical action (1831.) at the place of contact, does produce a current, and in the latter case a strong one. Or if any other of the contacts in the arrangement can produce a current, why is not that shown by some corresponding effect? The only answers are, to say, that the peculiar iron has the same electromotive properties and relations as platinum, or that the nitrous acid is included under the same law with the metals (1809. 1835.); and so the sum of the effects of all the contacts in the circuit is nought, or an exact balance of forces. That the iron is like the platinum in having no electromotive force at its contacts without chemical action, I believe; but that it is unlike it in its electrical relations, is evident from the difference between the two in strong nitric acid, as well as in weak acid; from their difference in the power of transmitting electric currents to either nitric acid or sulphuret of potassium, which is very great; and also by other differences. That the nitrous acid is, as to the power of its contacts, to be separated from other electrolytes and classed with the metals in what is, with them, only an assumption, is a gratuitous mode of explaining the difficulty, which will come into consideration, with the case of sulphuret of potassium, hereafter (1835. 1859. 1889. 2060.).

1845. To the electro-chemical philosopher, the case is only another of the many strong instances, showing that where chemical action is absent in the voltaic circuit, there no current can be formed; and that whether solution of sulphuret of potassium or nitrous acid be the electrolyte or connecting fluid used, still the results are the same, and contact is shown to be inefficacious as an active electromotive condition.

1846. I need not say that the introduction of different metals between the iron and platinum at their point of contact, produced no difference in the results (1833. 1834.) and caused no current; and I have said that heat and chemical action applied there produced their corresponding effects. But these parallels in action and non-action show the identity in nature of this circuit, (notwithstanding the production of the surface of peculiar iron on that metal,) and that with solution of sulphuret of potassium: so that all the conclusions drawn from it apply here; and if that case



ultimately stand firm as a proof against the theory of contact force, this will stand also.

1847. I now used oxide of iron and platinum as the extremes of the solid part of the circuit, and the nitrous acid as the fluid; i. e. I heated the iron wire in the flame of a spirit-lamp, covering it with a coat of oxide in the manner recommended by SCHÖENBEIN in his investigations, and then used it instead of the clean iron (1843.). The oxide of iron was at first in the least degree positive, and then immediately neutral. This circuit, then, like the former, gave no current at common temperatures; but it differed much from it in conducting power, being a very excellent conductor of a thermo current, the oxide of iron not offering that obstruction to the passage of the current which the peculiar iron did (1843. 1844.). Hence scale oxide of iron and platinum produce no current by contact, the third substance in the proof circuit being nitrous acid; and so the result agrees with that obtained in the former case, where that third substance was solution of sulphuret of potassium.

1848. In using nitrous acid it is necessary that certain precautions be taken, founded on the following effect. If a circuit be made with the green nitrous acid, platinum wires, and a galvanometer, in a few seconds all traces of a current due to first disturbances will disappear; but if one wire be raised into the air and instantly returned to its first position, a current is formed, and that wire is negative, across the electrolyte, to the other. If one wire be dipped only a small distance into the acid, as for instance one fourth of an inch, then the raising that wire not more than one eighth of an inch and instantly restoring it, will produce the same effect as before. The effect is due to the evaporation of the nitrous acid from the exposed wire (1937.). I may perhaps return to it hereafter, but wish at present only to give notice of the precaution that is required in consequence, namely, to retain the immersed wires undisturbed during the experiment.

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1849. Proceeding on the facts made known by SCHÖENBEIN respecting the relation of iron and nitric acid, I used that acid as the fluid in a voltaic circuit formed with iron and platinum. Pure nitric acid is so deficient in conducting power (1817.) that it may be supposed capable of stopping any current due to the effect of contact between the platinum and iron; and it is further objectionable in these experiments, because, acting feebly on the iron, it produces a chemically excited current, which may be considered as mingling its effect with that of contact: whereas the object at present is, by excluding such chemical action, to lay bare the influence of contact alone. Still the results with it are consistent with the more perfect ones already described; for in a circuit of iron, platinum, and nitric acid, the joint effects of the chemical action on the iron and the contact of iron and platinum, being to produce a current of a certain constant force indicated by the galvanometer, a little chemical action, brought into play where the iron and platinum were in contact as before (1831.), produced a

current far stronger than that previously existing. If then, from the weaker current, the part of the effect due to chemical action be abstracted, how little room is there to suppose that any effect is due to the contact of the metals.

1850. But a *red nitric acid* with platinum plates conducts a thermo current well, and will do so even when considerably diluted (1818.). When such red acid is used between iron and platinum, the conducting power is such, that one half of the permanent current can be overcome by a counter thermo current of bismuth and antimony. Thus a sort of comparison is established between a thermo current on the one hand, and a current due to the joint effects of chemical action on iron and contact of iron and platinum on the other. Now considering the admitted weakness of a thermo current, it may be judged what the strength of that part of the second current due to contact can, at the utmost, be; and how little it is able to account for the strong currents produced by ordinary voltaic combinations.

1851. If for a clean iron wire one oxidized in the flame of a spirit-lamp be used, being associated with platinum in pure strong nitric acid, there is a feeble current, the oxide of iron being positive to the platinum, and the facts mainly as with iron. But the further advantage is obtained of comparing the contact of strong and weak acid with this oxidized wire. If one volume of the strong acid and four volumes of water be mixed, this solution may be used, and there is even less deflection than with the strong acid: the iron side is now not sensibly active, except the most delicate means be used to observe the current. Yet in both cases if a chemical action be introduced in place of the contact, the resulting current passes well, and even a thermo current can be made to show itself as more powerful than any due to contact.

1852. In these cases it is safest to put the whole of the oxidized iron under the surface and connect it in the circle by touching it with a platinum wire; for if the oxidized iron be continued through from the acid to the air, it is almost certain to suffer from the joint action of the acid and air at their surface of contact.

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1853. I proceeded to use a fluid differing from any of the former: this was solution of *potassa*, which has already been employed by DE LA RIVE (1823.) with iron and platina, and which when strong has been found to be a substance conducting so well, that even a thermo current could pass it (1819.), and therefore fully sufficient to show a contact current, if any such exists.

1854. Yet when a strong solution of this substance was arranged with silver and platinum, (bodies differing sufficiently from each other when connected by nitric or muriatic acid,) as in the former cases, a very feeble current was produced, and the galvanometer-needle stood nearly at zero. The contact of these metals therefore did not appear to produce a sensible current; and, as I fully believe, because no electromotive power exists in such contact. When that contact was exchanged for a very feeble chemical action, namely, that produced by interposing a little piece of paper



moistened in dilute nitric acid (1831.), a current was the result. So here, as in the many former cases, the arrangement with a little chemical action and no metallic contact produces a current, but that without the chemical action and with the metallic contact produces none.

1855. Iron or nickel associated with platinum in this strong solution of potassa was positive. The force of the produced current soon fell, and after an hour or so was very small. Then annulling the metallic contact at *x*, fig. 2, and substituting a feeble chemical action there, as of dilute nitric acid, the current established by the latter would pass and show itself. Thus the cases are parallel to those before mentioned (1849, &c.), and show how little contact alone could do, since the effect of the conjoint contact of iron and platinum and chemical action of potash and iron were very small as compared with the contrasted chemical action of the dilute nitric acid.

1856. Instead of a strong solution of potassa, a much weaker one consisting of one volume of strong solution and six volumes of water was used, but the results with the silver and platinum were the same: no current was produced by the metallic contact as long as that only was left for exciting cause, but on substituting a little chemical action in its place (1831.), the current was immediately produced.

1857. Iron and nickel with platinum in the weak solution also produced similar results, except that the positive state of these metals was rather more permanent than with the strong solution. Still it was so small as to be out of all proportion to what was to be expected according to the contact theory.

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1858. Thus these different contacts of metals and other well-conducting solid bodies prove utterly inefficient in producing a current, as well when solution of potassa is the third or fluid body in the circuit, as when that third body is either solution of sulphuret of potassium, or hydrated nitrous acid, or nitric acid, or mixed nitric and nitrous acids. Further, all the arguments respecting the inefficacy of the contacts of bodies interposed at the junction of the two principal solid substances, which were advanced in the case of the sulphuret of potassium solution (1833.), apply here with potassa; as they do indeed in every case of a conducting circuit where the interposed fluid is without chemical action and no current is produced. If a case could be brought forward in which the interposed fluid is without action, is yet a sufficiently good conductor, and a current *is* produced; then, indeed, the theory of contact would find evidence in its favour, which, as far as I can perceive, could not be overcome. I have most anxiously sought for such a case, but cannot find one (1798.).

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1859. The argument is now in a fit state for the resumption of that important point before adverted to (1835. 1844.), which, if truly advanced by an advocate for the

contact theory, would utterly annihilate the force of the previous experimental results, though it would not enable that theory to give a reason for the activity of, and the existence of a current in, the pile: but which, if in error, would leave the contact theory utterly defenceless and without foundation.

1860. A supporter of the contact theory may say that the various conducting electrolytes used in the previous experiments are like the metals; i. e. that they have an electromotive force at their points of contact with the metals and other solid conductors employed to complete the circuit; but that this is of such consistent strength at each place of contact, that, in a complete circle, the sum of the forces is 0 (1809.). The actions at the contacts are tense electromotive actions, but balanced, and so no current is produced. But what experiment is there to support this statement? where are the measured electromotive results proving it (1808.)? I believe there are none.

1861. The contact theory after assuming that mere contacts of dissimilar substances have electromotive powers, further assumes a difference between metals and liquid conductors (1810.) without which it is impossible that the theory can explain the current in the voltaic pile: for whilst the contact effects in a metallic circuit are assumed to be always perfectly balanced, it is also assumed that the contact effects of the electrolytes or interposed fluid with the metals are not balanced, but are so far removed from anything like an equilibrium, as to produce most powerful currents, even the strongest that a voltaic pile can produce. If so, then why should the solution of sulphuret of potassium be an exception? it is quite unlike the metals: it does not appear to conduct without decomposition; it is an excellent electrolyte, and an excellent *exciting* electrolyte in proper cases (1880.), producing most powerful currents when it acts chemically; it is in all these points quite unlike the metals, and, in its action, like any of the acid or saline exciting electrolytes commonly used. How then can it be allowed that, without a single direct experiment, and solely for the purpose of avoiding the force of those which are placed in opposition, we should suppose it to leave its own station amongst the electrolytes, and class with the metals; and that too, in a point of character which, even with them, is as yet a mere assumption (1809.).

1862. But it is not with the sulphuret of potassium alone that this freedom must be allowed; it must be extended to the nitrous acid (1843. 1847.), to the nitric acid (1849, &c.), and even to the solution of potash (1854.); all these being of the class of electrolytes, and yet exhibiting no current in circuits where they do not occasion chemical action. Further, this exception must be made for *weak solutions* of sulphuret of potassium (1842.) and of potassa (1856.), for they exhibit the same phenomena as the stronger solutions. And if the contact theorists claim it for these weak solutions, then how will they meet the case of weak nitric acid which is not similar in its action on iron to strong nitric acid (1877.), but can produce a powerful current?



1863. The chemical philosopher is embarrassed by none of these difficulties; for he first, by a simple direct experiment, ascertains whether any of the two given substances in the circuit are active chemically on each other. If they are, he expects and finds the corresponding current; if they are not, he expects and he finds no current, though the circuit be a good conductor and he look carefully for it (1829.).

1864. Again; taking the case of iron, platina, and solution of sulphuret of potassium, there is no current; but for iron substitute zinc, and there is a powerful current. I might for zinc substitute copper, silver, tin, cadmium, bismuth, lead, and other metals; but I take zinc, because its sulphuret dissolves and is carried off by the solution, and so leaves the case in a very simple state: the fact, however, is as strong with any of the other metals. Now if the contact theory be true, and if the iron, platina, and solution of sulphuret of potassium give contacts which are in perfect equilibrium as to their electromotive force, then why does changing the iron for zinc destroy the equilibrium? Changing one metal for another in a metallic circuit causes no alteration of this kind: nor does changing one substance for another among the great number of bodies which, as solid conductors, may be used to form conducting (but chemically inactive) circuits (1867, &c.). If the solution of sulphuret of potassium is to be classed with the metals as to its action in the experiments I have quoted (1825, &c.), then, how comes it to act quite unlike them, and with a power equal to the *best* of the other class, in the new cases of zinc, copper, silver, &c. (1882. 1885, &c.).

1865. This difficulty, as I conceive, must be met, on the part of the contact theorists, by a new assumption, namely, that this fluid sometimes acts as the best of the metals, or first class of conductors, and sometimes as the best of the electrolytes or second class. But surely this would be far too loose a method of philosophizing in an experimental science (1889.); and further, it is most unfortunate for such an assumption, that this second condition or relation of it never comes on by itself, so as to give us a pure case of a current from contact alone; it never comes on *without* that chemical action to which the chemist so simply refers all the current which is then produced.

1866. It is unnecessary for me to say that the same argument applies with equal force to the cases where nitrous acid, nitric acid, and solution of potash are used; and it is supported with equal strength by the results which they have given (1843. 1849. 1853.).

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1867. It may be thought that it was quite unnecessary, but in my desire to establish contact electromotive force, to do which I was at one time very anxious, I made many circuits of three substances, including a galvanometer, all being conductors, with the hope of finding an arrangement which, without chemical action, should produce a current. The number and variety of these experiments may be understood

from the following summary ; in which metals, plumbago, sulphurets and oxides, all being conductors even of a thermo current, were thus combined in various ways :

- |                                  |                                      |
|----------------------------------|--------------------------------------|
| 1. Platinum.                     | 8. Native gray sulphuret of copper.  |
| 2. Iron.                         | 9. Native iron pyrites.              |
| 3. Zinc.                         | 10. Native copper pyrites.           |
| 4. Copper.                       | 11. Galena.                          |
| 5. Plumbago.                     | 12. Artificial sulphuret of copper.  |
| 6. Scale oxide of iron.          | 13. Artificial sulphuret of iron.    |
| 7. Native peroxide of manganese. | 14. Artificial sulphuret of bismuth. |

1 and 2 with 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, in turn.

1 and 3 with 5, 6, 7, 8, 9, 10, 11, 12, 13, 14.

1 and 5 with 6, 7, 8, 9, 10, 11, 12, 13, 14.

3 and 6 with 7, 8, 9, 10, 11, 12, 13, 14.

4 and 5 with 6, 7, 8, 9, 10, 11, 12, 13, 14.

4 and 6 with 7, 8, 9, 10, 11, 12, 13, 14.

4 and 7 with 8, 9, 10, 11, 12, 13, 14.

4 and 8 with 9, 10, 11, 12, 13, 14.

4 and 9 with 10, 11, 12, 13, 14.

4 and 10 with 11, 12, 13, 14.

4 and 11 with 12, 13, 14.

4 and 12 with 13, 14.

4 and 13 with 14.

1 and 4 with 12.

1868. MARIANINI states from experiment that copper is positive to sulphuret of copper\*: with the Voltaists, according to the same philosopher, sulphuret of copper is positive to iron (1878.), and with them also iron is positive to copper. These three bodies therefore ought to give a most powerful circle: but on the contrary, whatever sulphuret of copper I have used, I have found not the slightest effect from such an arrangement.

1869. As peroxide of lead is a body causing a powerful current in solution of sulphuret of potassium, and indeed in every case of a circuit where it can give up part of its oxygen, I thought it reasonable to expect that its contact with metals would produce a current, if contact ever could. A part of that which had been prepared (1822.), was therefore well dried, which is quite essential in these cases, and formed into the following combinations :

Platinum.	Zinc.	Peroxide of lead.
Platinum.	Lead.	Peroxide of lead.
Platinum.	Cadmium.	Peroxide of lead.
Platinum.	Iron.	Peroxide of lead.

\* Memoria della Società Italiana in Modena, 1827, xxi. 224.



Of these varied combinations, not one gave the least signs of a current, provided differences of temperature were excluded; though in every case the circle formed was, as to conducting power, perfect for the purpose, i. e. able to conduct even a very weak thermo current.

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1870. In the contact theory it is not therefore the metals alone that must be assumed to have their contact forces so balanced as to produce, in any circle of them, an effect amounting to nothing (1809.); but all solid bodies that are able to conduct, whether they be forms of carbon, or oxides, or sulphurets, must be included in the same category. So also must the electrolytes already referred to, namely, the solutions of sulphuret of potassium and potash, and nitrous and nitric acids, in every case where they do not act chemically. In fact *all conductors* that do not act chemically in the circuit must be assumed, by the contact theory, to be in this condition, until a case of voltaic current without chemical action is produced (1858.).

1871. Then, even admitting that the results obtained by VOLTA and his followers with the electrometer prove that mere contact has an electromotive force and can produce an effect, surely all experience with contact alone goes to show that the electromotive forces in a circuit are always balanced. How else is it likely that the above-named most varied substances should be found to agree in this respect? unless indeed it be, as I believe, that all substances agree in this, of having no such power at all. If so, then where is the source of power which can account by the theory of contact for the current in the voltaic pile? If they are not balanced, then where is the sufficient case of contact alone producing a current? or where are the numerical data which indicate that such a case can be (1808. 1868.)? The contact philosophers are bound to produce, not a case where the current is infinitesimally small, for such cannot account for the current of the voltaic pile, and will always come within the debatable ground which DE LA RIVE has so well defended, but a case and data of such distinctness and importance as may be worthy of opposition to the numerous cases produced by the chemical philosopher (1892.); for without them the contact theory as applied to the pile appears to me to have *no* support, and, as it asserts contact electromotive force even *with* the balanced condition, to be almost without foundation.

1872. To avoid these and similar conclusions, the contact theory must bend about in the most particular and irregular way. Thus the contact of solution of sulphuret of potassium with iron must be considered as balanced by the joint force of its contact with platinum, and the contact of iron and platinum with each other; but changing the iron for lead, then the contact of the sulphuret with the latter metal is no longer balanced by the other two contacts, it has all of a sudden changed its relation: after a few seconds, when a film of sulphuret has been formed by the chemical action, then the current ceases, though the circuit be a good conductor (1885.); and



now it must be assumed that the solution has acquired its first relation to the metals and to the sulphuret of lead, and gives an equilibrium condition of the contacts in the circle.

1873. So also with this sulphuretted solution and with potassa, dilution must, by the theory, be admitted as producing *no change* in the character of the contact force; but with nitric acid it, on the contrary, must be allowed to change the character of the force greatly (1977.). So again acids and alkalies (as potassa) in the cases where currents are produced by them, as with zinc and platinum for instance, must be assumed as giving the preponderance of electromotive force on the same side, though these are bodies which might have been expected to give opposite currents, since they differ so much in their nature.

1874. Every case of a current is obliged to be met, on the part of the contact advocates, by assuming powers at the points of contact, in *the particular case*, of such proportionate strengths as will consist with the results obtained, and the theory is made to bend about (1956. 1992. 2006. 2014. 2063.), having no general relation for the acids or alkalies, or other electrolytic solution used. The result therefore comes to this: The theory can predict nothing regarding the results; it is accompanied by no case of a voltaic current produced without chemical action, and in those associated with chemical action, it bends about to suit the real results, these contortions being exactly parallel to the variations which the pure chemical force, by experiment, indicates.

1875. In the midst of all this, how simply does the chemical theory meet, include, combine, and even predict, the numerous experimental results! When there is a current there is also chemical action; when the action ceases, the current stops (1882. 1885. 1894.); the action is determined either at the anode or the cathode, according to circumstances (2039. 2041.), and the direction of the current is invariably associated with the direction in which the active chemical forces oblige the anions and cations to move in the circle (962. 2052.).

1876. Now when in conjunction with these circumstances it is considered, that the many arrangements without chemical action (1825, &c.) produce no current; that those with chemical action almost always produce a current; that hundreds occur in which chemical action without contact produces a current (2017, &c.); and that as many with contact but without chemical action (1867.) are known and are inactive; how can we resist the conclusion, that the powers of the voltaic battery originate in the exertion of chemical force?

¶ iii. *Active circles excited by solution of sulphuret of potassium.*

1877. In 1812 DAVY gave an experiment to show, that of two different metals, copper and iron, that having the strongest attraction for oxygen was positive in oxidizing solutions, and that having the strongest attraction for sulphur was positive in

sulphuretted solutions\*. In 1827 DE LA RIVE quoted several such inversions of the states of two metals, produced by using different solutions, and reasoned from them, that the mere contact of the metals could not be the cause of their respective states, but that the chemical action of the liquid produced these states†.

1878. In a former paper I quoted Sir HUMPHRY DAVY's experiment (943.), and gave its result as a proof that the contact of the iron and copper could not originate the current produced; since when a dilute acid was used in place of the sulphuret, the current was reverse in direction, and yet the contact of the metals remained the same. M. MARIANINI‡ adds, that copper will produce the same effect with tin, lead, and even zinc; and also that silver will produce the same results as copper. In the case of copper he accounts for the effect by referring it to the relation of the iron and the new body formed on the copper, the latter being, according to VOLTA, positive to the former§. By his own experiment the same substance was negative to the iron across the same solution||.

1879. I desire at present to resume the class of cases where a solution of sulphuret of potassium is the liquid in a voltaic circuit; for I think they give most powerful proof that the current in the voltaic battery cannot be produced by contact, but is due altogether to chemical action.

1880. The solution of sulphuret of potassium (1812.) is a most excellent conductor of electricity (1814.). When subjected between platinum electrodes to the decomposing power of a small voltaic battery, it readily gave pure sulphur at the anode, and a little gas, which was probably hydrogen, at the cathode. When arranged with platinum surfaces so as to form a RITTER's secondary pile, the passage of a feeble primary current, for a few seconds only, makes this secondary battery effective in causing a counter current; so that, in accordance with electrolytic conduction (923. 1343.), it probably does not conduct without decomposition, or if at all, its point of electrolytic intensity (966. 983.) must be very low. Its exciting action (speaking on the chemical theory) is either the giving an anion (sulphur) to such metallic and other bodies as it can act upon, or, in some cases, as with the peroxides of lead and manganese, and the protoxide of iron (2046.), the abstraction of an anion *from* the body in contact with it, the current produced being in the one or the other direction accordingly. Its chemical affinities are such, that in many cases its anion goes to that metal, of a pair of metals, which is left untouched when the usual exciting electrolytes are employed; and so a beautiful inversion of the current in relation to the metals is obtained; thus, when copper and nickel are used with it, the anion goes to the copper; but when the same metals are used with the ordinary electrolytic fluids, the anion goes to the nickel. Its excellent conducting power renders

\* Elements of Chemical Philosophy, p. 148.

† Annales de Chimie, 1828, xxxvii. 231-237; xxxix. 299.

‡ Memorie della Società Italiana in Modena, 1837, xxi. p. 224.

§ Ibid. p. 219.

|| Ibid. p. 224.



the currents it can excite very evident and strong; and it should be remembered that the strength of the resulting currents, as indicated by the galvanometer, depends jointly upon the energy (not the mere quantity) of the exciting action called into play, and the conductive ability of the circuit through which the current has to run. The value of this exciting electrolyte is increased for the present investigation, by the circumstance of its giving, by its action on the metals, resulting compounds, some of which are insoluble, whilst others are soluble; and, of the insoluble results, some are excellent conductors, whilst others have no conducting power at all.

1881. The experiments to be described were made generally in the following manner. Wires of platinum, gold, palladium, iron, lead, tin, and the other malleable metals, about one twentieth of an inch in diameter and six inches long, were prepared. Two of these being connected with the ends of the galvanometer-wires, were plunged at the same instant into the solution of sulphuret of potassium in a test-glass, and kept there without agitation (1919.), the effects at the same time being observed. The wires were in every case carefully cleansed with fresh fine sand-paper and a clean cloth; and were sometimes even burnished by a glass rod, to give them a smooth surface. Precautions were taken to avoid any difference of temperature at the junctions of the different metals with the galvanometer-wires.

1882. *Tin and platinum*.—When tin was associated with platinum, gold, or, I may say, any other metal which is chemically inactive in the solution of the sulphuret, a strong electric current was produced, the tin being positive to the platinum through the solution, or, in other words, the current being from the tin through the solution to the platinum. In a very short time this current fell greatly in power, and in ten minutes the galvanometer-needle was nearly at 0°. On then endeavouring to transmit the antimony-bismuth thermo current (1825.) through the circuit, it was found that it could not pass, the circle having lost its conducting power. This was the consequence of the formation on the tin of an insoluble, investing, non-conducting sulphuret of that metal; the non-conducting power of the body formed is not only evident from the present result, but also from a former experiment (1821.).

1883. MARIANINI thinks it is possible that (in the case of copper, at least (1878.), and so, I presume, for all similar cases, for surely one law or principle should govern them,) the current is due to the contact force of the sulphuret formed. But that application is here entirely excluded; for how can a *non-conducting* body form a current, either by contact or in any other way? No such case has ever been shown, nor is it in the nature of things; so that it cannot be the contact of the sulphuret that here causes the current; and if not in the present, why in any case? for nothing happens here that does not happen in any other instance of a current produced by the same exciting electrolyte.

1884. On the other hand, how beautiful a proof the result gives in confirmation of the chemical theory! Tin can take sulphur from the electrolyte to form a sulphuret; and whilst it is doing so, and in proportion to the degree in which it is doing so, it



produces a current; but when the sulphuret which is formed, by investing the metal, shuts off the fluid and prevents further chemical action, then the current ceases also. Nor is it *necessary* that it should be a non-conductor for this purpose, for conducting sulphurets will perform the same office (1885. 1894.), and bring about the same result. What, then, can be more clear, than that whilst the sulphuret is *being formed* a current is produced, but that when formed its mere contact can do nothing towards such an effect?

1885. *Lead*.—This metal presents a fine result in the solution of sulphuret of potassium. Lead and platinum being the metals used, the lead was at first highly positive, but in a few seconds the current fell, and in two minutes the galvanometer-needle was at  $0^{\circ}$ . Still the arrangement conducted a feeble thermo current extremely well, the conducting power not having disappeared, as in the case of tin; for the investing sulphuret of lead is a conductor (1820.). Nevertheless, though a conductor, it could stop the further chemical action; and that ceasing, the current ceased also.

1886. Lead and gold produced the same effect. Lead and palladium the same. Lead and iron the same, except that the circumstances respecting the tendency of the latter metal under common circumstances to produce a current from the electrolyte to itself, have to be considered and guarded against (1826. 2049.). Lead and nickel also the same. In all these cases, when the lead was taken out and washed, it was found beautifully invested with a thin polished pellicle of sulphuret of lead.

1887. With lead, then, we have a *conducting* sulphuret formed, but still there is no sign that its contact can produce a current, any more than in the case of the *non-conducting* sulphuret of tin (1882.). There is no new or additional action produced by this *conducting* body; there was no deficiency of action with the former *non-conducting* product; both are alike in their results, being, in fact, essentially alike in their relation to that on which the current really depends, namely, an active chemical force. A piece of lead put *alone* into the solution of sulphuret of potassium, has its surface converted into sulphuret of lead, the proof thus being obtained, even when the current cannot be formed, that there is a force (chemical) present and active under such circumstances; and such force can produce a current of chemical force when the circuit form is given to the arrangement. The force at the place of excitement shows itself, both by the formation of sulphuret of lead and the production of a current. In proportion as the formation of the one decreases the production of the other diminishes, though all the bodies produced are conductors, and contact still remains to perform any work or cause any effect to which it is competent.

1888. It may perhaps be said that the current is due to the contact between the solution of sulphuret and the lead, (or tin, as the case may be,) which occurs at the beginning of the experiment; and that when the action ceases, it is because a new body, the sulphuret of lead, is introduced into the circuit, the various contacts being then balanced in their force. This would be to fall back upon the assumption before

resisted (1861. 1865. 1872.), namely, that the solution may class with metals and such-like bodies, giving balanced effects of contact in relation to *some* of these bodies, as in this case, to the sulphuret of lead produced, but not with *others*, as the lead itself; both the lead and its sulphuret being in the same category as the metals generally (1809. 1870.).

1889. The utter improbability of this as a natural effect, and the absence of all experimental proof in support of it, have been already stated (1861. 1871.), but one or two additional reasons against it now arise. The state of things may perhaps be made clearer by a diagram or two, in which assumed contact forces may be assigned, in the absence of all experimental expression, without injury to the reasoning. Let fig. 4. Plate III. represent the electromotive forces of a circle of platinum, iron, and solution of sulphuret of potassium; or platinum, nickel, and solution of sulphuret; cases in which the forces are, according to the contact theory, balanced (1860.). Then fig. 5 may represent the circle of platinum, lead, and solution of sulphuret, which does produce a current, and, as I have assumed, with a resulting force of 11  $\longrightarrow$ . This in a few minutes becomes quiescent, i. e. the current ceases, and fig. 6 may represent this new case according to the contact theory. Now is it at all likely that by the intervention of sulphuret of lead at the contact *c*, fig. 5, and the production of two contacts *d* and *e*, fig. 6, such an enormous change of the contact force suffering alteration should be made as from 10 to 21? the intervention of the same sulphuret either at *a* or *b* (1834. 1840.) being able to do nothing of the kind, for the sum of the force of the two new contacts is in that case exactly equal to the force of the contact which they replace, as is proved by such interposition making no change in the effects of the circle (1867. 1840.). If therefore the intervention of this body between *lead* and platinum at *a*, or between solution of *sulphuret of potassium* and platinum at *b* (fig. 5.) causes no change, these cases including its contact with both lead and the solution of sulphuret, is it at all probable that its intervention between these two bodies at *c* should make a difference equal to double the amount of force previously existing, or indeed any difference at all?

1890. Such an alteration as this in the sum assigned as the amount of the forces belonging to the sulphuret of lead by virtue of its two places of contact, is equivalent I think to saying that it partakes of the anomalous character already supposed to belong to certain fluids, namely, of sometimes giving balanced forces in circles of good conductors, and at other times not (1865.).

1891. Even the metals themselves must in fact be forced into this constrained condition; for the effect at a point of contact, if there be *any at all*, must be the result of the *joint* and *mutual actions* of the bodies in contact. If therefore in the circuit, fig. 5, the contact forces are not balanced, it must be because of the deficient *joint* action of the lead and solution at *c*\*. If the metal and fluid were to act in their

\* My numbers are assumed, and if other numbers were taken, the reasoning might be removed to contact *b*, or even to contact *a*, but the end of the argument would in every case be the same.



proper character, and as iron or nickel would do in the place of the lead, then the force there would be — 21, whereas it is less, or according to the assumed numbers only  $\leftarrow$  10. Now as there is no reason why the lead should have any superiority assigned to it over the solution, since the latter can give a balanced condition amongst good conductors in its proper situation as well as the former; how can this be, unless lead possess that strange character of sometimes giving equipoised contacts, and at other times not (1865.).

1892. If that be true of lead, it must be true of all the metals which, with this sulphuretted electrolyte, give circles producing currents; and this would include bismuth, copper, antimony, silver, cadmium, zinc, tin, &c. &c. With other electrolytic fluids iron and nickel would be included, and even gold, platinum, palladium; in fact all the bodies that can be made to yield in any way active voltaic circuits. Then is it possible that this can be true, and yet not a single combination of this extensive class of bodies be producible that can give the current without chemical action (1867.), considered not as a result, but as a known and pre-existing force?

1893. I will endeavour to avoid further statement of the arguments, but think myself bound to produce (1799.) a small proportion of the enormous body of facts which appear to me to bear evidence all in one direction.

1894. *Bismuth*.—This metal when associated with platinum, gold, or palladium in solution of the sulphuret of potassium, gives active circles, the bismuth being positive. In the course of less than half an hour the current ceases; but the circuit is still an excellent conductor of thermo currents. Bismuth with iron or nickel produces the same final result with the reservation before made (1826.). Bismuth and lead give an active circle; at first the bismuth is positive; in a minute or two the current ceases, but the circuit still conducts the thermo current well.

1895. Thus whilst sulphuret of bismuth is in the act of formation the current is produced; when the chemical action ceases the current ceases also; though contact continues and the sulphuret be a good conductor. In the case of bismuth and lead the chemical action occurs at both sides, but is most energetic at the bismuth, and the current is determined accordingly. Even in that instance the cessation of chemical action causes the cessation of the current.

1896. In these experiments with *lead* and *bismuth* I have given their associations with platinum, gold, palladium, iron, and nickel; because, believing in the first place that the results prove all current to depend on chemical action, then, the quiescent state of the resulting or final circles shows that the contacts of these metals in their respective pairs are *without force* (1829.): and upon that again follows the passive condition of all those contacts which can be produced by interposing other conducting bodies between them (1833.); an argument that need not again be urged.

1897. *Copper*.—This substance being associated with platinum, gold, iron, or any metal chemically inactive in the solution of sulphuret, gives an active circle, in which the copper is positive through the electrolyte to the other metal. The action, though



it falls, does not come to a close as in the former cases, and for these simple reasons; that the sulphuret formed is not compact but porous, and does not adhere to the copper, but separates from it in scales. Hence results a continued renewal of the chemical action between the metal and electrolyte, and a continuance of the current. If after a while the copper plate be taken out and washed, and dried, even the wiping will remove part of the sulphuret in scales, and the nail separates the rest with facility. Or if a copper plate be left in abundance of the solution of sulphuret, the chemical action *continues*, and the coat of sulphuret of copper becomes thicker and thicker.

1898. If, as MARIANINI has shown\*, a copper plate which has been dipped in the solution of sulphuret, be removed before the coat formed is so thick as to break up from the metal beneath, and be washed and dried, and then replaced, in association with platinum or iron, in the solution, it will at the first be neutral, or, as is often the case, negative (1827. 1838.) to the other metal, a result quite in opposition to the idea, that the mere presence of the sulphuret on it could have caused the former powerful current and positive state of the copper (1897. 1878.). A further proof that it is not the mere *presence*, but the *formation*, of the sulphuret which causes the current, is, that, if the plate be left long enough for the solution to penetrate the investing crust of sulphuret of copper and come into activity on the metal beneath, then the plate becomes active, and a current is produced.

1899. I made some sulphuret of copper, by igniting thick copper wire in a Florence flask or crucible in abundance of vapour of sulphur. The body produced is in an excellent form for these experiments, and a good conductor; but it is not without action on the sulphuretted solution, from which it can take more sulphur, and the consequence is, that it is positive to platinum or iron in such a solution. If such sulphuret of copper be left long in the solution, and then be washed and dried, it will generally acquire the final state of sulphuration, either in parts or altogether, and also be inactive, as the sulphuret formed on the copper was before (1898.); i. e. when its chemical action is exhausted, it ceases to produce a current.

1900. *Native gray sulphuret of copper* has the same relation to the electrolyte: it takes sulphur from it and is raised to a higher state of combination; and, as it is also a conductor (1820.), it produces a current, being itself positive so long as the action continues.

1901. But when the copper is *fully sulphuretted*, then all these actions cease; though the sulphuret be a conductor, the contacts still remain, and the circle can carry with facility a feeble thermo current. This is not only shown by the quiescent cases just mentioned (1898.), but also by the utter inactivity of platinum and *compact yellow copper pyrites*, when conjoined by this electrolyte, as shown in a former part of this paper (1840.)

1902. *Antimony*.—This metal, being put alone into a solution of sulphuret of potassium, is acted on, and a sulphuret of antimony formed, which does not adhere

\* Memorie della Società Italiana in Modena, 1837, xxi. 224.

strongly to the metal, but wipes off. Accordingly if a circle be formed of antimony, platinum, and the solution, the antimony is positive in the electrolyte, and a powerful current is formed, which continues. Here then is another beautiful variation of the conditions under which the chemical theory can so easily account for the effects, whilst the theory of contacts cannot. The sulphuret produced in this case is a non-conductor whilst in the solid state (402.); it cannot therefore be that any contact of this sulphuret can produce the current; in that respect it is like the sulphuret of tin (1882.). But that circumstance does not stop the occurrence of the chemical current; for, as the sulphuret forms a porous, instead of a continuous crust, the electrolyte has access to the metal and the action goes on.

1903. *Silver*.—This metal associated with platinum, iron, or other metals inactive in this electrolyte, is strongly positive, and gives a powerful continuous current. Accordingly, if a plate of silver, coated with sulphuret by the simple action of the solution, be examined, it will be found that the crust is brittle and broken, and separates almost spontaneously from the metal. In this respect, therefore, silver and copper are alike, and the action consequently continues in both cases; but they differ in the sulphuret of silver being a nonconductor (434.) for these feeble currents, and, in that respect, this metal is analogous to antimony (1902.).

1904. *Cadmium*.—Cadmium with platinum, gold, iron, &c., gives a powerful current in the solution of sulphuret, and the cadmium is positive. On several occasions this current continued for two or three hours or more; and at such times, the cadmium being taken out, washed, and wiped, the sulphuret was found to separate easily in scales on the cloth used.

1905. Sometimes the current would soon cease; and then the circle was found not to conduct the thermo current (1813.). In these cases, also, on examining the cadmium, the coat of sulphuret was strongly adherent, and this was more especially the case when prior to the experiment the cadmium, after having been cleaned, was burnished by a glass rod (1881.). Hence it appears that the sulphuret of this metal is a non-conductor, and that its contact could not have caused the current (1883.) in the manner MARIANINI supposes. All the results it supplies are in perfect harmony with the chemical theory and adverse to the contact theory.

1906. *Zinc*.—This metal, with platinum, gold, iron, &c., and the solution of sulphuret, produces a very powerful current, and is positive through the solution to the other metal. The current was permanent. Here another beautiful change in the circumstances of the general experiment occurs. Sulphuret of zinc is a non-conductor of electricity (1821.), like the sulphurets of tin, cadmium, and antimony; but then it is soluble in the solution of sulphuret of potassium; a property easily ascertainable by putting a drop of solution of zinc into a portion of the electrolytic solution, and first stirring them a little, by which abundance of sulphuret of zinc will be formed; and then stirring the whole well together, when it will be redissolved. The consequence of this solubility is, that the zinc when taken out of the solution is perfectly free from



investing sulphuret of zinc. Hence, therefore, a very sufficient reason, on the chemical theory, why the action should go on. But how can the theory of contact refer the current to any contact of the metallic sulphuret, when that sulphuret is, in the first place a non-conductor, and, in the next, is dissolved and carried off into the solution at the moment of its formation?

1907. Thus all the phenomena with this admirable electrolyte (1880.), whether they be those which are related to it as an active (1879.) or as a passive (1825, &c.) body, confirm the chemical theory, and oppose that of contact. With tin and cadmium it gives an impermeable non-conducting body; with lead and bismuth it gives an impermeable conducting body; with antimony and silver it produces a permeable non-conducting body; with copper a permeable conducting body; and with zinc a soluble non-conducting body. The chemical action and its resulting current are perfectly consistent with all these variations. But try to explain them by the theory of contact, and, as far as I can perceive, that can only be done by twisting the theory about and making it still more tortuous than before (1861. 1865. 1872. 1874. 1889.); special assumptions being necessary to account for the effects which, under it, become so many special cases.

1908. *Solution of protosulphuret of potassium, or bihydrosulphuret of potassa.*—I used a solution of this kind as the electrolyte in a few cases. The results generally were in accordance with those already given, but I did not think it necessary to pursue them at length. The solution was made by passing sulphuretted hydrogen gas for twenty-fours through a strong solution of pure caustic potassa.

1909. Iron and platinum with this solution formed a circle in which the iron was first negative, then gradually became neutral, and finally acquired a positive state. The solution first acted as the yellow sulphuret in reducing the investing oxide (2049.), and then, apparently, directly on the iron, dissolving the sulphuret formed. Nickel was positive to platinum from the first, and continued so though producing only a weak current. When weak chemical action was substituted for metallic contact at *x*, fig. 2 (1831.), a powerful current passed. Copper was highly positive to iron and nickel; as also to platinum, gold, and the other metals which were unacted upon by the solution. Silver was positive to iron, nickel, and even lead; as well as to platinum, gold, &c. Lead is positive to platinum, then the current falls, but does not cease. Bismuth is also positive at first, but after a while the current almost entirely ceases, as with the yellow sulphuret of potassium (1894.).

1910. Native gray sulphuret of copper and artificial sulphuret of copper (1899.) were positive to platinum and the inactive metals: but yellow copper pyrites, yellow iron pyrites, and galena, were inactive with these metals in this solution; as before they had been with the solution of yellow or bisulphuret of potassium. This solution, as might be expected from its composition, has more of alkaline characters in it than the yellow sulphuret of potassium.

1911. Before concluding this account of results with the sulphuretted solutions, as



exciting electrolytes, I will mention the varying and beautiful phenomena which occur when copper and silver, or two pieces of copper, or two pieces of silver, form a circle with the yellow solution. If the metals be copper and silver, the copper is at first positive and the silver remains untarnished; in a short time this action ceases, and the silver becomes positive; at the same instant it begins to combine with sulphur and becomes covered with sulphuret of silver; in the course of a few moments the copper again becomes positive; and thus the action will change from side to side several times, and the current with it, according as the circumstances become in turn more favourable at one side or the other.

1912. But how can it be thought that the current first produced is due in any way to the *contact* of the sulphuret of copper formed, since its presence there becomes at last the reason why that first current diminishes, and enables the silver, which is originally the weaker in exciting force, and has no sulphuret as yet formed on it, to assume for a time the predominance, and produce a current which can overcome that excited at the copper (1911.)? What can account for these changes, but chemical action? which, as it appears to me, accounts, as far as we have yet gone, with the utmost simplicity, for *all* the effects produced, however varied the mode of action and their circumstances may be.

*Royal Institution,*  
*December 12, 1839.*







